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Electronic spectra of tetraazatetrahedrane(N_4) isomers

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Abstract : MRINDO/S calculations augmented by singly excited configuration interaction were performed on the isomers of tetraazatetrahedrane(N_4). In this work we considered two isomers of N_4 which belong to D_{2h} and C_{2v} symmetry. These isomers are metastable and hence the interpretation of their spectra seems to be important. We report ionization potentials, allowed singlet excitations, the corresponding triplet excitations, and the singlet triplet splittings in each isomer. Rydberg excitations are also interpreted.

Keywords : N_4 isomers, ionization potentials, electronic spectra.

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1. Introduction

Metastability is a term usually assigned with a thermodynamically unstable form of some molecules that nevertheless, have a reasonable lifetime in that form. Molecules in electronic excited states that are prohibited by selection rules from decaying to lower states *via* processes such as phosphorescence offer one example of metastability. Another type which we can term geometric metastability, is due to a particular arrangement of the atoms in a molecule. In a sense, all molecules which can be formed in endothermic reactions are metastable relative to their simpler components, which means they represent a local minimum on the potential energy surface while some other atomic arrangement constitutes the global minimum. Often however, such molecules have long lifetimes and can be described by conventional chemical bonding concepts. In other cases, we have unusual geometrically metastable species. Such molecules should have some electronic basis for their existence, but because of other competing forces, they have never been observed [1].

The potential existence of more exotic metastable species offers insight into the nature of the chemical bond. For example, the normal form of phosphorus is P_4 while that of nitrogen is N_2, although N_4 has the same qualitative valence bond description. P_4 is more stable than $2P_2$ since P_2 has a relatively weak bond, while the N_2 bond is one of the strongest known. This does not indicate N_4 as a possible molecule but does imply that it is likely to be metastable [1].

Lauderdale *et al* [1] studied the bonding and stability of N_4. They opine that synthesis of metastable molecules would offer a potential route toward the storage of large amount of energy. The evolving quest for more efficient explosive and rocket propellant has led to the examination of new and novel ways of storing energy [2].

While the potential nitrogen molecules (N_4, N_6 and N_8) have been studied in past [3–9], their electronic spectra

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were not accounted for. So in this work, we considered N_4 isomers to account for their electronic spectra. We hope that the results reported here would be helpful in further theoretical or experimental investigations. The method employed in the present work, can be found in Ref. [10].

The optimized geometries of N_4 isomers which were determined and characterized at the correlated level by Lauderdale *et al* [1], were used in this work.

2. Results

Table 1 contains ionization potentials deduced from Koopmans' theorem [11] and the corresponding orbital symmetries. Table 2 contains transition energies of allowed singlets, oscillator strengths, and symmetries of the excited states. The last column of Table 2 contains the percentages Rydberg character of the states. Table 3 gives transition energies of the triplets, symmetries of the excited states, and singlet-triplet splitting. The last column of Table 3 gives the percentage Rydberg character of the states.

Table 1. The lowest ionization potentials o tetraazatetrahedrane(eV).

Molecule (Symmetry)	MRINDO/S I.P.	Symmetry of orbital	Type
N_4	11.07	b_{1u}	
(D_{2h})	11.72	b_{1g}	π
	12.21	b_{3u}	σ
	14.76	a_g	σ
	14.96	b_{2u}	π
	17.74	a_g	σ
	18.07	b_{2g}	σ
	24.64	b_{1u}	σ
	29.08	b_{3u}	σ
	42.07	a_g	σ
N_4	10.11	b_2	σ
(C_{2v})	11.68	b_1	π
	14.47	a_1	σ
	15.03	a_1	σ
	15.27	a_1	σ
	15.72	b_1	π
	20.57	a_1	σ
	23.37	b_2	σ
	32.05	a_1	σ
	40.86	a_1	σ

Table 2. The allowed singlet excitations in tetraazatetrahedrane. All energies are in eV.

Molecule (Symmetry)	MIRINDO/S Transition energy	f	Sym. of exc. state	Type of transition	%Rydberg character N
N_4	5.00	0.035	B_{1u}	$n\rightarrow\pi^*$	0
(D_{2h})	6.38	0.019	B_{1u}	$n\rightarrow\sigma^*$	0
	6.75	0.083	B_{1u}	$n\rightarrow\sigma^*$	5
	7.92	0.015	B_{3u}	$n\rightarrow\sigma_R^*$	96
	8.22	0.191	B_{3u}	$n\rightarrow\sigma^*$	13
	8.23	0.458	B_{1u}	$n\rightarrow\pi^*$	4
	9.04	0.002	B_{3u}	$n\rightarrow\sigma_R^*$	99
N_4	2.49	0.006	B_2	$n\rightarrow\sigma^*$	0
(C_{2v})	3.48	0.034	B_2	$n\rightarrow\pi^*$	0
	4.04	0.003	A_1	$n\rightarrow\sigma^*$	0
	5.75	0.113	A_1	$n\rightarrow\pi^*$	0
	6.59	0.052	B_2	$n\rightarrow\pi^*$	0
	6.77	0.081	A_1	$n\rightarrow\sigma^*$	1
	8.14	0.023	B_2	$n\rightarrow\sigma^*$	4
	8.53	0.012	A_1	$n\rightarrow\sigma_R^*$	97
	8.68	0.435	A_1	$n\rightarrow\sigma^*$	6
	8.78	0.014	B_2	$n\rightarrow\sigma_R^*$	97
	9.14	0.203	B_1	$n\rightarrow\sigma^*$	1

Table 3. Triplet excitations in tetraazatetrahedrane*. All energies are in eV.

Molecule (Symmetry)	MIRINDO/S Transition energy		Sym. of exc. state	Type of transition	%Rydberg character N
N_4	1.63	3.37	B_{1u}	$n\rightarrow\pi^*$	0
(D_{2h})	4.80	1.95	B_{3u}	$n\rightarrow\sigma^*$	0
	5.52	2.81	B_{1u}	$n\rightarrow\pi^*$	0
	6.07	0.31	B_{1u}	$n\rightarrow\sigma^*$	0
	6.98	1.24	B_{3u}	$n\rightarrow\sigma^*$	17
	7.91	0.01	B_{1u}	$n\rightarrow\sigma_R^*$	100
	9.03	0.01	B_{3u}	$n\rightarrow\sigma_R^*$	99
N_4	1.00	2.48	B_2	$n\rightarrow\pi^*$	0
(C_{2v})	2.25	0.24	B_2	$n\rightarrow\sigma^*$	0
	2.86	2.89	A_1	$n\rightarrow\pi^*$	0
	3.35	0.69	A_1	$n\rightarrow\sigma^*$	0
	5.19	1.40	B_2	$n\rightarrow\pi^*$	0
	6.23	0.54	A_1	$n\rightarrow\sigma^*$	1
	6.75	1.93	A_1	$n\rightarrow\sigma^*$	0
	7.16	1.98	B_1	$n\rightarrow\sigma^*$	0
	7.71	0.43	B_2	$n\rightarrow\sigma^*$	0
	8.52	0.01	A_1	$n\rightarrow\sigma_R^*$	100
	8.77	0.01	B_2	$n\rightarrow\sigma_R^*$	100

* These triplet excitations correspond to their respective allowed singlet excitations.

3. Discussion

3.1. Ionization potentials :

The first ionization potential of both the isomers is interpreted as the removal of an electron from an in-plane σ orbital while the second one as the removal of an electron from an out-of-plane π orbital. It is worthwhile to notice that the first σ electron to be removed from $C_{2v}N_4$ requires less energy than that from $D_{2h}N_4$ while the second σ electron to be removed from $C_{2v}N_4$ requires much more energy than that from $D_{2h}N_4$. Again, the last electron to be removed from $C_{2v}N_4$ requires less energy (40.86 eV) than that from $D_{2h}N_4$ (42.07 eV). Thus, we find no definite trend of variation in ionization potentials of the isomers.

3.2. Singlet excitations :

(i) $D_{2h}N_4$

The present calculations predict that most of the low-lying singlet-singlet and singlet-triplet transitions in $D_{2h}N_4$ are almost entirely valence shell transitions. The contribution of Rydberg orbitals to some excited states is moderate but much stronger Rydberg contributions come into play at higher energies. This is also true in $C_{2h}N_4$.

The first absorption in $D_{2h}N_4$ occurs at about 5.00 eV. The transition corresponding to this absorption is assigned as $n\rightarrow\pi^*$ which has an oscillator strength amounting to 0.035. The next absorption takes place at about 6.38 eV and the transition corresponding to this absorption is assigned as $n\rightarrow\sigma^*$ which has an oscillator strength amounting to 0.019. Analyzing the spectrum of $D_{2h}N_4$ we infer that the $n\rightarrow\pi^*$ transitions are more intense than the $n\rightarrow\sigma^*$ ones. The maximum absorption in $D_{2h}N_4$ occurs at about 8.23 eV. The transition corresponding to the maximum absorption is assigned as $n\rightarrow\pi^*$ which has an oscillator strength amounting to 0.458. We predict that all the allowed transitions in $D_{2h}N_4$ can be observed experimentally since they are adequately spaced and exhibit considerable intensity. Only the observation of the $n\rightarrow\sigma^*$ transition at 8.22 eV may cause difficulty since it lies in the vicinity of the most intense $n\rightarrow\pi^*$ transition at 8.23 eV. However, these two transitions can be differentiated and characterized on the basis of their polarizations; the former is *x*-polarized while the latter *z*-polarized.

The spectrum of $D_{2h}N_4$ consists of *ns* and *np* Rydberg series converging upon the first ionization potential at 11.07 eV. The *ns* Rydberg series consists of only one member at 7.29 eV which has a quantum defect of 0.92. The *np* Rydberg series consist of six members, the one at 9.04 eV is symmetry allowed and has a quantum defect of 0.41. These two allowed Rydberg transitions, which lie apart from the other intense bands, can be easily observed experimentally.

(ii) $C_{2v}N_4$

The first absorption in $C_{2v}N_4$ takes place at about 2.49 eV. The transition corresponding to this absorption is a weak (f = 0.006) $n\rightarrow\sigma^*$. An $n\rightarrow\pi^*$ transition at 3.48 eV is relatively strong (f = 0.034). Nevertheless, contray to $D_{2h}N_4$, the $n\rightarrow\sigma^*$ transitions are found dominant in $C_{2v}N_4$. The most intense (f = 0.435) transition in $C_{2v}N_4$ is assigned as $n\rightarrow\sigma^*$ at 8.68 eV. Thus, this energy corresponds to the maximum absorption in $C_{2v}N_4$. Similar to $D_{2h}N_4$, the bands in $C_{2v}N_4$ are adequately spaced and hence can be easily observed experimentally.

It is worthwhile to notice that the two allowed Rydberg transitions (see Table2) in $C_{2v}N_4$, correspond to the members of *nd* Rydberg series and converge upon the first ionization potential at 10.11 eV. The former member at 8.53 eV is less intense (f = 0.012) than the latter (f = 0.014) at 8.78 eV, their respective quantum defects being 0.07 and 0.05. Both these members are *z*-polarized. Our calculation reveals that the spectrum of $C_{2v}N_4$ consists of *ns* and *np* Rydberg series, but the members of these series are too weak ($f \sim 10^{-6}$) and show no polarization. Thus, we note a marked difference between the spectra of $C_{2v}N_4$ and $D_{2h}N_4$.

3.3. Triplet excitations :

The $n\rightarrow\pi^*$ transitions in both the isomers exhibit intensity. The S-T splits of $n\rightarrow\pi^*$ transitions in both the isomers are higher than those of $n\rightarrow\sigma^*$ ones. It is interesting to note that the S-T splits of the Rydberg excitations in both the isomers are the same.

4. Conclusion

The electronic spectra of the isomers have not yet been observed or theoretically calculated. The ground- as well as the excited-state properties reported here will be forthcomming. The structural features of the spectra of the isomers are well pronounced under the present calculation. We hope that the present results would be helpful in further studies.

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